

## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
12 September 2003 (12.09.2003)

PCT

(10) International Publication Number  
**WO 03/074092 A1**(51) International Patent Classification<sup>7</sup>: **A61L 2/04**,  
A23L 3/02, 3/10, B65B 55/10, A23B 4/005, A23C 3/023,  
A61L 2/26

(21) International Application Number: PCT/JP03/02431

(22) International Filing Date: 3 March 2003 (03.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
JP2002-57629 4 March 2002 (04.03.2002) JP(71) Applicant (*for all designated States except US*):  
**KUREHA CHEMICAL INDUSTRY COMPANY, LIMITED** [JP/JP]; 1-9-11, Nihonbashi Horidome-cho,  
Chuo-ku, Tokyo 103-8552 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **YAMANE, Kazuyuki** [JP/JP]; c/o KUREHA CHEMICAL INDUSTRY COMPANY, LIMITED, 16, Ochiai, Nishiki-machi, Iwaki-shi, Fukushima 974-8686 (JP). **KAWAKAMI, Yukichika** [JP/JP]; c/o KUREHA CHEMICAL INDUSTRY COMPANY, LIMITED, 16, Ochiai, Nishiki-machi, Iwaki-shi, Fukushima 974-8686 (JP). **WAKAMATSU, Akiko** [JP/JP]; c/o KUREHA CHEMICAL INDUSTRY COMPANY, LIMITED, 16, Ochiai, Nishiki-machi, Iwaki-shi, Fukushima 974-8686 (JP). **YASUDA, Matsuo** [JP/JP]; c/o FOOD SCIENCE LABORATORIES, KUREHA CHEMICAL INDUSTRY COMPANY,LIMITED, 18-13, Oaza Kamitamari, Tamari-mura, Niihari-gun, Ibaraki 311-3436 (JP). **TANAKA, Mikio** [JP/JP]; c/o FOOD SCIENCE LABORATORIES, KUREHA CHEMICAL INDUSTRY COMPANY, LIMITED, 18-13, Oaza Kamitamari, Tamari-mura, Niihari-gun, Ibaraki 311-3436 (JP).(74) Agent: **ENDO, Yukio**; TOKYO INTERNATIONAL PATENT FIRM, 2nd Floor, Miyata Building, 17-16, Nishishimbashi 1-chome, Minato-ku, Tokyo 105-0003 (JP).(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF HEAT-TREATING PACKAGED PRODUCT AND HEAT-TREATED PACKAGED PRODUCT

(57) Abstract: ABSTRACT A packaged product formed by enclosing a content material, such as food or beverage, sanitary products or medical products, within a packaging material including at least a layer of hydrophilic resin, is heat-treated with hot water for, e.g., boil sterilization or retort sterilization. The hot water is caused to contain a water-soluble compound in an amount substantially exceeding a level contained in tap water, whereby it becomes possible to suppress the opalescence of the packaging material causing inferior appearance or transparency and leading to a lowering in gas-barrier property, which has been problematic in the conventional boil or retort hot water treatment.

## DESCRIPTION

METHOD OF HEAT-TREATING PACKAGED PRODUCT  
AND HEAT-TREATED PACKAGED PRODUCT

## [TECHNICAL FIELD]

5           The present invention relates to a method of  
heat-treating a packaged product (formed by  
packaging a content material, such as food,  
beverages, sanitary products or medical materials,  
with a plastic packaging material or container for  
10 packaging or containing the content material) with  
hot water for sterilization, cooking, etc. More  
particularly, the present invention relates to a  
method of heat-treating a packaged product with a  
plastic material or container (hereinafter inclusively  
15 referred to as a "packaging material") in hot water  
while suppressing opalescence (or whitening) or  
lowering in gas-barrier property of the plastic  
packaging material, and also a packaged product  
thus heat-treated.

## 20 [BACKGROUND ART]

Hitherto, plastic packaging materials have been  
widely used for packaging or as containers for food  
or beverage, sanitary products and medical materials.  
Among such plastic packaging materials, some  
25 materials have been known as causing opalescence or  
a lowering in transparency after a heat treatment  
when such a packaging material is heat-treated by

itself or in a form of a packaged product enclosing,  
e.g., food or a medical material for the purpose of  
sterilization and/or cooking at a temperature on the  
order of 60-140°C within tap water or industrial  
5 water. (Industrially, a heat-treatment using hot water  
at 60-100°C is frequently called a boiling treatment,  
and one using hot water above 100°C is frequently  
called a retort treatment.) The opalescence of the  
packaging material causes problems, such as limited  
10 observation of the content material state, and poor  
appearance, and is sometimes accompanied with a  
lowering in gas-barrier property. The lowering in  
gas-barrier property of the packaging material  
results in problems, such as shortage of shelf-life of  
15 the packaged product. There has not yet been  
developed an effective method for alleviating the  
above-mentioned problems accompanying the  
heat-treatment of packaged products in hot water.

## 20 [DISCLOSURE OF INVENTION]

An object of the present invention is to provide  
a method of heat-treating a packaged product with a  
plastic material with hot water while suppressing the  
opalescence of the packaging material causing a poor  
25 appearance and a limited clarity and further leading  
to a lowering in gas-barrier property.

Another object of the present invention is to

provide a packaged product with a plastic material and thus heat-treated.

The present invention, provides a heat-treating method for a packaging product, comprising:

- 5 providing a packaging product formed by enclosing a comparative examples within a packaging material comprising at least a layer of hydrophilic resin, and heat-treating the packaging product with hot water, wherein the hot water is caused to contain a
- 10 water-soluble compound.

The present invention further provides a packaging product heat-treated by the above-mentioned heat-treating method.

- 15 Including a preferred laminate state of the packaging material, the present invention further provides a heat-treated packaged product, comprising a heat-treated packaging material having a multi-layer structure including an inner layer of a hydrophilic gas-barrier resin layer selected from the
- 20 group consisting of ethylene-vinyl alcohol copolymer and glycolic acid (co-)polymer, and a content material enclosed within the packaging material, wherein the heat-treated packaging material has a haze below 20%.

- 25 Some details of history of our study with the above objects through which we have arrived at the present invention will be referred to below.

We have studied the opalescence due to hot-water treatment of a plastic packaging material causing disadvantage in appearance and transparency, and recognized that the opalescence is attributable to at least a hydrophilic resin layer contained in the packaging material. More specifically, if a hydrophilic resin layer is present in the packaging material to be treated with hot water, hot water molecules are caused to contact the hydrophilic resin layer not only in the case where the hydrophilic resin layer constitutes a surface layer of the packaging material directly contacting the hot water, as a matter of course, but also in the case where it constitutes an inner layer which does not directly contact the hot water due to coverage with a hydrophobic resin layer (including an inner surface layer not contacting the hot water in addition to an intermediate layer between two surface layers), due to diffusion of hot water molecules through microscopic pores in or through gaps between hydrophobic polymer molecules constituting the surface layer, thereby reaching the hydrophilic resin layer to whiten the hydrophilic resin layer by forming a cluster of water molecules attached to the hydrophilic resin layer, according to our understanding. In this instance, if the hydrophilic resin is also hydrolyzable, the opalescence is

promoted in association with a molecular weight-decreasing effect due to the hydrolyzation, and if the hydrophilic resin layer forms a surface layer, the molecules causing the surface layer is partially dissolved to cause a surface roughening which also promotes the opalescence. These opalescence-promoting phenomena are further enhanced by an increase in hot water temperature reflecting an increase in kinetic energy of water molecules and therefore are more noticeably caused in the retort treatment using hot water at a temperature exceeding 100°C than in the boiling treatment using hot water temperature at a temperature of at most 100°C.

However, the above-mentioned opalescence during hot-water treatment of a packaging material including a hydrophilic resin layer has been recognized as an inevitable phenomenon accompanying the use of a hydrophilic resin.

Accordingly, it has been an actual practice to obviate the use of a packaging material including a hydrophilic resin layer for a packaged product subjected to a boiling or retort hot water treatment in spite of the fact that many hydrophilic resin layers are known to have excellent properties, inclusive of gas-barrier property.

In contrast thereto, we had an idea that if the

percentage of free water molecules is lowered to decrease the kinetic energy of the water molecules by adding a water-soluble compound in hot water to cause hydration thereof with the water molecules, the  
5 above-mentioned opalescence of a packaging material including a hydrophilic resin layer might be suppressed. Based on the concept, we have experimentally confirmed that the addition of a water-soluble compound in the hot-water treatment  
10 exhibits a remarkable opalescence-suppression effect, thereby arriving at the present invention.

#### [DETAILED DESCRIPTION OF THE INVENTION]

The plastic packaging material used in the  
15 present invention may comprise either a single-layered film or container comprising one hydrophilic resin layer, or a multi-layered film or container comprising at least two resin layers including at least one hydrophilic resin layer.

20 The film-form packaging material may comprise, e.g., a non-stretched film, a stretched film, a heat-shrinkable film, or a non-heat-shrinkable film.

Such a film may, for example, be produced by melt-extrusion of a plastic material through a flat  
25 die.

A non-stretched film may be produced by melt-extrusion, followed by shaping into a final film

form at a relatively high temperature in the course of cooling. A stretched film or a heat-shrinkable film may, for example, be produced through a process wherein a sheet formed by melt-extrusion is

5 stretched while being cooled, or is cooled, re-heated and stretched, optionally followed by heat-setting. For the film formation, a sheet may be melt-extruded through a flat die and then stretched uniaxially, successively biaxially or simultaneously biaxially by

10 the roller process, the tenter process or a combination of these. Alternatively, it is also possible to effect biaxial stretching by the inflation process using a circular die. The film after the stretching may be subjected to heat-shrinkability

15 adjustment for providing a heat shrinkability of zero or a desired degree by an appropriate annealing treatment under no tension or application of an appropriate degree of tension.

As described above, the film may comprise a

20 single layer of hydrophilic resin or may be formed into a multi-layer structure together with another resin layer. The multilayer formation may be effected by lamination, coating or co-extrusion.

The lamination may include: wet lamination, dry

25 lamination, extrusion lamination, hot melt lamination, non-solvent lamination, etc., which may be selectively used as desired. The coating may



include: provision of a moisture-proof coating or a moisture-proof lamination layer which may be selectively used as desired.

A flat film or a film formed by slitting of an inflation film of a large lay-flat width may be formed into a bag, a pouched., filled with a content material, such as foods, sanitary products or medical materials and hermetically sealed, before being subjected to hot water treatment according to the present invention.

The filling and packaging of a content material may also be effected by using an automatic packaging machine, by which a film is formed into a tube by center seaming while filling the tube with a content material, such as food, to package the content material.

Examples of the packaging material in the form of a container may include: trays or cups formed by subjecting a plastic sheet of a single layer or multi-layers to sheet-forming technique, such as vacuum forming or pressure forming, and bottles formed by blow molding.

Similarly as the films, these containers may be subjected to the hot water treatment according to the present invention after being filled with a content material.

Examples of the hydrophilic resin giving the

hydrophilic resin layer of the packaging material may include: polyamides; polyesters; polyorganic acids, such as polyamino acids; vinyl alcohol (co-)polymers, and acid-modified olefin (co-)polymers, and the

5 degree of hydrophilicity suitable to be treated according to the method of the present invention may be judged based on the intended effect depending on whether or not the film is opacified when subjected to an ordinary hot water treatment. More

10 specifically, when an, e.g.,  $50\mu$  m-thick single-layered film of a hydrophilic resin is subjected to a test of immersion in still hot water at  $100^{\circ}\text{C}$  for 30 min., if the film is hydrolyzed ( the hydrophilic resin layer should be disposed as an inner layer in

15 this case) or exhibits a haze value of 20% or higher (that is the degree of opalescence to be prevented according to the present invention), a packaging material including the hydrophilic resin layer may be a suitable object to be treated by the hot water.

20 treatment method according to the present invention. According to this standard, aromatic polyesters do not generally come under hydrophilic resins, but aliphatic polyesters generally come under hydrophilic resins. Incidentally, it is also possible to use a

25 mixture of two or more species of hydrophilic resins, or a mixture of at least one species of hydrophobic resin and at least one species of hydrophilic resin.

Also, in this case, the required degree of hydrophilicity can be judged according to the above-mentioned hot water immersion test.

For providing a packaging material of multi-layer structure, the above-mentioned hydrophilic resin layer may be laminated with a surface layer (outer surface layer) which may comprise a hydrophilic resin free from hydrolyzability selected from the above-mentioned class of hydrophilic resins or also a hydrophobic resin. Preferred examples thereof may include: polyolefins or olefin copolymers, such as polyethylene and polypropylene; aromatic polyesters, such as polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate; (aliphatic or aromatic) polyamides; and styrene resins comprising homopolymer and copolymers of styrene. These surface layer resins may be used singly or in mixture of two or more species, and can also be suitably used as a resin constituting an inner layer (i.e., an intermediate layer or an inner surface layer).

In a preferred embodiment of the present invention, a gas-barrier resin layer is included as a hydrophilic resin layer. This embodiment is preferred because a heat-treatment method, as by boiling or retorting, is frequently used for sterilizing

a packaged product enclosing a content material such as food, and such a content material is preferably enclosed with a packaging material including an (oxygen) gas-barrier resin layer for long-term

5 preservation thereof, whereas many resins showing good gas-barrier property are hydrophilic.

[Hydrophilic gas-barrier resin layer]

Preferred examples of hydrophilic gas-barrier resin may include: glycolic acid (co-)polymer(PGA),  
10 ethylene-vinyl alcohol copolymer (EVOH), polyvinyl alcohol, and polyamide (co-)polymer. These hydrophilic gas-barrier resins are described below in some detail.

Glycolic acid (co-)polymer (PGA)

15 A hydrophilic gas-barrier resin particularly preferably used in the present invention is glycolic acid (co-)polymer. The reason is that glycolic acid (co-)polymer exhibits extremely excellent gas-barrier property and moisture-barrier property but its use in  
20 a packaging material subjected to boiling or retort sterilization has been restricted because of its high hydrophilicity (or hydrolyzability) causing opalescence during the heat-treatment thereof by boiling or retorting, whereas the problem can be  
25 effectively solved by the present invention.

Glycolic acid (co-)polymer preferably used in the present invention is crystalline and has a melting

point. Such a glycolic acid (co-)polymer may be produced by polycondensation of glycolic acid or an ester or salt thereof, or by ring-opening polymerization of glycolide which is a bimolecular cyclic ester of glycolic acid as represented by a reaction formula shown below. Particularly, in order to produce a glycolic acid (co-)polymer for providing a formed product, such as a sheet or a film, expected to show a high strength, the latter ring-opening polymerization of glycolide is preferred.

15

By using glycolide alone, glycolic acid homopolymer can be obtained. By using glycolide and a smaller amount of another comonomer within a extent of retaining the crystallinity, i.e., within an range of retaining a melting point, a glycolic acid copolymer can be obtained. Examples of the comonomer may include: cyclic monomers, inclusive of ethylene oxalate (i.e., 1,4-dioxane-2,3-dione); lactide; and lactones, such as  $\beta$ -propiolactone,  $\beta$ -butyrolactone, pivalolactone,  $\gamma$ -butyrolactone,  $\delta$

25

-valerolactone,  $\beta$ -methyl- $\delta$ -valerolactone, and  $\epsilon$ -caprolactone; trimethylene carbonate, and 1,3-dioxane; hydroxycarboxylic acids, such as lactic acid, 3-hydroxypropanoic acid, 3-hydroxybutanoic acid, 4-hydroxybutanoic acid and hydroxycaproic acid, and their alkyl esters; substantially equal molar mixtures of aliphatic diols, such as ethylene glycol and 1,4-butane diol with aliphatic dicarboxylic acids, such as succinic acid and adipic acid, and their alkyl esters; and combinations of two or more species of such co-monomers. As a starting material for polymerization, it is also possible to use a combination of glycolide and glycolic acid.

Among these comonomers, cyclic monomers, such as lactide, caprolactone and trimethylene carbonate; and hydroxycarboxylic acids, such as lactic acid and glycolic acid, are preferred, because of easy copolymerizability and capability of providing copolymers having excellent physical properties. Such a comonomer is used in a proportion of ordinarily at most 45 wt.%, preferably at most 30 wt.%, more preferably at most 10wt.%. The reason is that a copolymer having lost crystallinity is liable to result in remarkable lowering in properties, such as heat-resistance, gas-barrier property and mechanical strength.

A polymerization apparatus for providing such a

crystalline glycolic acid (co-)polymer may appropriately be selected from various apparatus including those of an extruder-type, a vertical type having paddle blades, a vertical type having helical ribbon blades, a laterally disposed extruder or kneader type, an ampoule-type, and a tube-type.

Other preferable hydrophilic gas-barrier resins are described below.

Ethylene-vinyl alcohol copolymer (EVOH)

Ethylene-vinyl alcohol copolymer (EVOH) used in the present invention may preferably have an ethylene content of 20-60mol% and a saponification degree of at least 95mol%. Such ethylene-vinyl alcohol copolymer is generally sold commercially and readily available.

Polyamide (PA)

As a polyamide, MXD6 nylon (polymetaxylylene adipamide) is preferred.

In the case of providing a multi-layered packaging material, it is possible to insert an optional intermediate layer between two surface layers. An example thereof is the above-mentioned hydrophilic gas-barrier resin layer (which however can also be a surface layer). In addition thereto, it is also possible to insert one or more layers of various resin material for the purpose of adjusting the strength, improving the inter-layer adhesion, etc.

Such an intermediate layer may preferably be formed of an extrudable resin material.

Examples of resins constituting such an adhesive resin layer may include: carboxylated  
5 polyolefin, epoxidized polyolefin, ethylene-vinyl acetate copolymer, ionomer, polyurethane, epoxy resin, styrene-butadiene-styrene copolymer (SBS), styrene-ethylene-butadiene-styrene copolymer (SEBS), polychloroprene, styrene-butadiene copolymer rubber  
10 (SBR), and natural rubber (NR).

The carboxylated polyolefin is a polyolefin having a carboxyl group introduced thereinto by modifying a polyolefin with an unsaturated acid monomer, such as acrylic acid, methacrylic acid, or  
15 maleic anhydride. The introduction of a carboxylic group may be effected either by copolymerization or grafting. The above mentioned unsaturated acid monomer can also be used in combination with a vinyl monomer, such as methacrylate esters, acrylate  
20 esters, or vinyl acetate.

The epoxidized polyolefin is a polyolefin having an epoxy group introduced thereinto by modifying a polyolefin with an epoxy group-containing monomer, such as glycidyl methacrylate. The introduction of  
25 an epoxy group may be effected either by copolymerization or grafting. The epoxy group-containing monomer can also be used in



combination with a vinyl monomer, such as methacrylate esters, acrylate esters, or vinyl acetate.

Among the above-mentioned adhesive resins, carboxylated polyolefin, epoxidized polyolefin and  
5 ethylene-vinyl acetate copolymer, are particularly preferred in view of the adhesiveness and processability. A mixture of these adhesive resins can also be used, as desired, within an extent of not adversely affecting the clarity of the resultant  
10 packaging material.

Including the respective layers described above, the packaging material forming the packaged product of the present invention may generally have a total thickness of 10-3000  $\mu$  m, of which the hydrophilic  
15 resin layer may preferably occupy 2 to 30%, while different thicknesses may be adopted depending on the form of the packaging material, such as sheets or containers (including bottles). In this instance, in the case of a relatively long container, such as a  
20 bottle, the above-mentioned thicknesses are taken at its body part, and in some cases, the hydrophilic resin layer may be present only at the body part and not present at the mouth or/and the bottom. In the case of inserting an adhesive resin layer, its  
25 thickness may preferably be selected from the range of ca. 0.5 to 100  $\mu$  m.

According to the present invention, a packaging

product is formed by enclosing a content material in the above-provided packaging material and is brought into contact with hot water containing a water-soluble compound, preferably by immersion, to effect a heat treatment.

The water-soluble compound may be either an inorganic electrolyte or a water-soluble organic compound.

The inorganic electrolyte can be an acid or an alkali so as to attain an intended effect of preventing the opalescence of the packaging material, but may preferably be a water-soluble inorganic salt from the view point of safe use. Preferred examples thereof may include: sodium chloride, potassium chloride, magnesium chloride, calcium chloride, aluminum chloride, and sodium sulfate. Among these, chlorides inclusive of sodium chloride, potassium chloride and magnesium chloride are preferably used.

As the water-soluble organic compound, organic acids, ethers and ketones, can be used; and in addition thereto, water-soluble alcohols, such as ethyl alcohol, ethylene glycol and polyethylene glycol are suitably used.

Among the above-mentioned water-soluble compounds, sodium chloride is most suitably used in view of the sanitary aspect and water-solubility.

As for the concentration of the water-soluble

compound in hot water, a higher concentration tends to exhibit a higher opalescence-prevention effect, but even a concentration of 1 wt.% exhibits a sufficient effect (Examples 2,3 and 5 described later), and a  
5 concentration of 0.1 wt.% or higher is expected to exhibit some effect for some hydrophilic resin. In this regard, it should be noted that the effective concentration level is different depending on the species of hydrophilic resin used, and even the  
10 concentration of 0.1 wt.% is substantially higher than a salt concentration (ca. 400 ppm(=0.04 wt.%)) or below that is allowed to be present in tap water which has been conventionally used for boil sterilization, etc., and is a level of concentration  
15 that cannot be realized unless a salt is intentionally added.

Through the hot-water treatment of the present invention using hot water containing a water-soluble compound, the resultant hot water-treated packaging  
20 film can be provided with a suppressed opalescence, as represented by a lowering in haze of preferably at least 10%, more preferably 20% or higher, compared with the case wherein the hot-water treatment is performed by using hot water treatment is performed  
25 by using hot water to which such a water-soluble compound has not been added. The concentration of a specific water-soluble compound to be added may

be determined so as to achieve the above-mentioned opalescence-suppression effect.

The hot-water treatment of the present invention can be achieved by using tap water with a water-soluble compound dissolved therein, instead of  
5 ordinary tap water, in a hot-water boiled sterilization apparatus or a hot-water retort sterilization apparatus which has been conventionally used.

The hot-water treatment time may be  
10 approximately set in the same manner as in the conventional treatment depending on the size of the content material and the level of sterilization intended by the boil sterilization or retort sterilization. For example, the treatment time may  
15 ordinarily range from 1 min. (surface sterilization of the content material to ca. 3 hours for a boil sterilization, and from 5 min. to ca. 1 hour for a retort sterilization.

If a packaging material provided with a  
20 heat-shrinkability through a stretching treatment is used as the packaging material, the packaging material causes a heat-shrinkage to tightly adhere to the content material during the hot-water treatment, thereby providing a heat-treatment packaging product  
25 exhibiting a further improved transparency.

#### [Examples]

Hereinbelow, the present invention will be

described more specifically based on Examples,  
Comparative examples and Reference examples.

Component resins used in the following  
Examples are represented by abbreviations or  
5 symbols in Tables appearing hereinafter, and the  
meanings thereof are described as follows:

- EVOH: ethylene-vinyl alcohol copolymer  
("SOANOL E3803B", made by Nippon Gosei Kagaku  
K.K.)
- 10 • Ny6-66: nylon 6-66 copolymer ("AMILAN CM6001XF",  
made by Toray K.K.)
- Ad.1: Adhesive 1=acid-modified LLDPE  
(linear low-density polyethylene)("ADMER NF528",  
made by Mitsui Kagaku K.K.)
- 15 • LLDPE: linear low-density polyethylene  
("MOATEC VO398CN", made by Idemitsu Sekiyu  
Kagaku K.K.)
- Ny6: nylon 6 ("AMILAN CM1021FS4", made by Toray  
K.K.)
- 20 • VLDPE: very low-density polyethylene ("MOATEC  
VO398CN", made by Idemitsu Sekiyu Kagaku K.K.)
- CPP: direct inflation film of propylene-ethylene  
random copolymer (made by Kureha Kagaku Kogyo  
K.K.)
- 25 • Ad.2: Adhesive 2= urethane-based adhesive for dry  
lamination.
- HB-NY: Ny6 (5  $\mu$  m)/MXD6(5  $\mu$  m)/NY6 (5  $\mu$  m)

co-extruded film ("SUPERNEAL SPR8H", made by Mitsubishi Kagaku Kohjin Packs K.K.)

• EVA: ethylene-vinyl acetate copolymer ("EVAFLEX V-527-4", made by Mitsui Dupont K.K.)

5 • PP: polypropylene ("NOVATEC FY6C", made by Nippon Polychem K.K.)

• Ad.3: Adhesive 3= malic acid-modified ethylene-vinyl acetate copolymer ("ADMER VF500", made by Mitsui Kagaku K.K.)

10 • Ad.4: Adhesive 4= maleic acid-modified polypropylene ("ADMER QB550", made by Mitsui Kagaku K.K.)

• Ad.5: ethylene-glycidyl methacrylate copolymer ("REXPEARL RA3150", made by Nippon Polyolefin K.K.)

15 • PGA: polyglycolic acid (made by Kureha Kagaku Kogyo K.K., specific gravity=1.6)

• Ny11: nylon 11 ("RILSAN BESVOAFDA", made by Atochem Co.)

[Examples 1-7, Comparative Examples 1-7]

20       As genuine working examples, a packaging product formed by enclosing a content material within a packaging material should be heat-treated. However, as the effect of boil or retort sterilization itself on the content material is well known to a  
25 skilled artisan, the opalescence characteristics of packaging film materials under boil or retort heat-treatment conditions were tested in the

following manner.

Two film samples each measuring 5 cm×5 cm was cut out from each of film-form plastic packaging materials having laminate structures shown in Table 1. (Note: In the following description including Tables, films having a laminate structure using "/" between layers are laminate films formed by co-extrusion, and films having a laminate structure using "|" between layers (of Example 4 and Comparative Example 4) are laminate films formed by dry lamination.). Each film sample of 5 cm×5 cm was enclosed within a pouch of polyethylene-laminated aluminum sheet measuring 12 cm×12 cm together with 10 ml of 25 wt.% sodium chloride aqueous solution (Examples 1-7) or tap water (Comparative Examples 1-6), and the pouch was hermetically sealed without leaving air therein. Two pouches prepared from each packaging material sample were immersed in hot water at 95°C and 120°C, respectively, for 0.5 hour, then cooled with tap water, and opened to take out the film samples. The film samples were then subjected to measurement of haze (according to JIS K6714). The measured results are shown in Table 1 together with haze values before the heat treatment. Incidentally, the heat treatment at 100°C was effected by immersion in hot water under the atmospheric pressure, and the

heat treatment at 120°C was by immersion in hot water in a retort oven. Further, the films of Examples 2,3 and 5 were also subjected to the boil and/or retort heat treatment in 1 %-saline water, and the measured haze values are indicated in parentheses in parallel in the following table 1. The films of Examples 1, 2 and 5 were also subjected to the boil and/or retort heat treatment in 0.5%-saline water and the measured values are indicated in parallel in (( )) (double parentheses) in the following Table 1.



Table 1

Example	Laminate structure (thickness : in $\mu\text{m}$ )	Total thickness ( $\mu\text{m}$ )	Haze (%) <sup>*</sup>		
			Before heat treatment	After heat treatment	
				98°C × 0.5hr	120°C × 0.5hr
1	EVOH/Ny6-66/Ad.1/LLDPE (43) (18) (18) (101)	180	2	19 ((51))	66 ((74))
Comp.1	ditto		2	77	89
2	Ny6/Ny6-66/Ad.1/LLDPE (36) (10) (15) (59)	120	5	10	14 (13),((28))
Comp.2	ditto		5	11	71
3	LLDPE/Ad.1/Ny6-66/Ad.1/VLDPE (36) (6) (43) (6) (59)	150	6	5 (8)	7 (23)
Comp.3	ditto		6	14	61
4	CPP/Ad.2/HB-Ny/CPP (15) (2) (15) (15)	49	5	7	19
Comp.4	ditto		5	11	45
5	EVA/Ad.3/EVOH/Ad.4/PP (40) (3) (24) (3) (30)	100	9	16 (13),((18))	13
Comp.5	ditto		9	40	92
6	PE/Ad.5/PGA/Ad.5/PE (60) (15) (50) (15) (60)	200	4	20	20
Comp.6	ditto		4	82	93
7	Ny6-66/Ad.1/LLDPE (46) (15) (59)	120	6	8	9
Comp.7	ditto		6	18	79

\* The haze values indicated in parentheses for Examples 2, 3 and 5 were obtained in the case of immersion in 1%-saline water; the haze values indicated in (( )) were obtained in the case of immersion in 0.5%-saline water; and the other haze values were obtained in the case of immersion in 25%-saline water.

#### [Example 8 and Comparative Example 8]

Two film-form plastic packaging material samples each having a laminate structure shown in Table 2 below were subjected to the same treatments as in the above Examples 1-7 and Comparative Examples 1-7, including: cutting-out of film samples, enclosures within pouches, heat treatment at 98°C for 0.5 hour and 3.0 hours, and measurement of haze values before and after the heat treatment. The results are also shown in Table 2.

Table 2

Example	Laminate structure ( thickness : in $\mu\text{m}$ )	Total thickness ( $\mu\text{m}$ )	Haze (%)		
			Before heat treatment	After heat treatment	
				98°C × 0.5hr	98°C × 3hrs
8	VLDPE/Ad.5/PGA/Ad.5/VLDPE	200	3	15	32
	(60) (15) (50) (15) (60)				
Comp.8	ditto		3	72	59

[Example 9, 10 and Comparative Example 9]

An EVOH-based laminate film ("PAIRFLEX

5 SHEET FA-292N", made by Kureha Kagaku Kogyo K.K.; total thickness = 200  $\mu\text{m}$ ) having a laminate structure shown below was immersed in tap water and saturated sodium chloride (saline) water (having a concentration of ca. 27wt.%) and subjected to

10 heat-treatments under conditions shown in Table 3. The states (particularly transparency) of the films after the immersion were evaluated by eye observation, and the results are also shown in Table

3.

15 Ny11/Ad.3/EVOH/Ny6-66/Ad.3/LLDPE/VLDPE

Thickness (25) (15) (15) (40) (15) (75) (15)  
( $\mu\text{m}$ )

Table 3

Example	Heating medium	Heating temp. (°C)	Heating time		
			1 hour	2 hours	4 hours
Com.9	tap water	100	opaque	opaque	opaque
9	sat. saline water	105	transparent	transparent	transparent
10	sat. saline water	120	transparent	a little turbid	a little turbid

[Reference Examples]

A polyglycolic acid-based laminate film having a  
5 laminate structure shown below was subjected to  
immersion in heating media shown in Table 4 at  
100°C for indicated periods of time, and then taken  
out to be observed with eyes with respect to  
appearances, particularly with respect to  
10 transparency. The results are shown in Table 4.

VLDPE/Ad.5/PGA/Ad.5/VLDPE  
(60) (15) (50) (15) (60)

15 Evaluation by eye observation:

The evaluation results shown in Table 4 were  
obtained by evaluation with eyes of appearances and  
shown in Table 4 at 5 levels of opacity according to  
the following standard:

20 A: None. ( Haze  $\leq$  10%, A level of haze obtained after  
heat-treating the laminate film for 1 hour in a drying  
oven at 100 °C.)

B: Slight. (Haze=10-20%),

C: Moderate. (Haze=20-50%),

25 D: Much. (Haze=50-80%),

E: Extreme. (Haze  $\geq$  80%).

Table 4

Heating medium *	Heating time		
	0.5 hr	1.0 hr	3.0 hrs
Pure water	C	D	E
sat. NaCl aq. (ca.27%)	A	A	A
25% NaCl aq.	A	A	A
15% NaCl aq.	A	A	A
5% NaCl aq.	B	B	C
sat. MgCl <sub>2</sub> aq. (ca.35%)	A	A	A
10% MgCl <sub>2</sub> aq.	B	B	C
sat. CaCl <sub>2</sub> aq. (ca.37%)	A	A	A
20% CaCl <sub>2</sub> aq.	A	A	A
5% CaCl <sub>2</sub> aq.	B	B	C
sat. KCl aq. (ca.22%)	A	A	A
10% KCl aq.	B	B	C
sat. Na <sub>2</sub> SO <sub>4</sub> aq. (ca.33%)	A	A	A
15% Na <sub>2</sub> SO <sub>4</sub> aq.	B	C	D
100% ethylene glycol aq.	A	A	A
50% ethylene glycol aq.	A	A	B
10% ethylene glycol aq.	B	B	D

\* The following abbreviations are used.

sat. : saturated

aq. : aqueous solution

#### [INDUSTRIAL APPLICABILITY]

As is understood from the above-described Examples, Comparative Examples and Reference  
 5 examples, according to the heat-treating method for a packaging product of the present invention, the conventional boil hot water treatment or retort hot water treatment is subjected to a simple modification of causing the hot water to contain a water-soluble  
 10 compound, whereby it becomes possible to remarkably suppress the opalescence of a packaging material causing disadvantage in appearance and

transparency and also a lowering in gas-barrier property, encountered in the conventional boil hot water treatment or retort hot water treatment of a packaging product with a packaging material

5 including a hydrophilic resin layer.

## CLAIMS:

1. A heat-treating method for a packaging product, comprising:

providing a packaging product formed by  
5 enclosing a content material within a packaging material comprising at least a layer of hydrophilic resin, and

heat-treating the packaging product with hot water,

10 wherein the hot water is caused to contain a water-soluble compound.

2. A heat-treating method according to Claim 1, wherein the hot water has a temperature of 60-100°C  
15 to effect a boiling heat-treatment.

3. A heat-treating method according to Claim 1, wherein the hot water has a temperature exceeding 100°C to effect a retort heat-treatment.

20

4. A heat-treating method according to any of Claim 1 to 3, wherein the hot water contains the water-soluble compound at a concentration exceeding 0.1 wt.%.  
25

5. A heat-treating method according to any of Claims 1 to 3, wherein the hot water contains the

water-soluble compound at a concentration of at least 1 wt.%.

6. A heat-treating method according to any of  
5 Claims 1 to 5, wherein the water-soluble compound is an inorganic electrolyte.

7. A heat-treating method according to Claim 6,  
wherein the water-soluble compound is a  
10 water-soluble inorganic salt.

8. A heat-treating method according to Claim 7,  
wherein the water-soluble compound is a chloride  
selected from the group consisting of sodium chloride,  
15 magnesium chloride, and potassium chloride.

9. A heat-treating method according to Claim 8,  
wherein the water-soluble compound is sodium  
chloride.

20

10. A heat-treating method according to any of  
Claims 1 to 5, wherein the water-soluble compound is  
a water-soluble organic compound.

25 11. A heat-treating method according to Claim  
10, wherein the water-soluble compound is a  
water-soluble alcohol.

12. A heat-treating method according to any of Claims 1 to 11, wherein the hydrophilic resin layer is a gas-barrier resin layer.

5

13. A heat-treating method according to Claim 12, wherein the gas-barrier resin is selected from the group consisting of ethylene-vinyl alcohol copolymer, polyamide (co-)polymers, and aliphatic ester

10 (co-)polymers.

14. A heat-treating method according to Claim 13, wherein the gas-barrier resin is selected from the group consisting ethylene-vinyl alcohol copolymer, polymetaxylylene adipamide and glycolic acid (co-)polymer.

15

15. A heat-treating method according to any of Claims 1 to 14, wherein the packaging material has a multi-layer structure.

20

16. A heat-treating method according to Claim 15, wherein the hydrophilic resin layer is disposed as a surface layer contacting the hot water of the packaging material.

25

17. A heat-treating method according to Claim



15, wherein the hydrophilic resin layer is disposed as an inner layer not directly contacting the hot water of the packaging material.

5           18. A heat-treating method according to Claim 17, wherein the gas-barrier resin is glycolic acid (co-)polymer.

10           19. A packaged product, which has been heat-treated by a heat-treating method according to any one of Claims 1 to 18.

15           20. A packaged product according to Claim 19, wherein the heat-treated packaging material has a haze below 20%.

20           21. A heat-treated packaged product, comprising a heat-treated packaging material having a multi-layer structure including an inner layer of a hydrophilic gas-barrier resin layer selected from the group consisting of ethylene-vinyl alcohol copolymer and glycolic acid (co-)polymer, and a content material enclosed within the packaging material, wherein the heat-treated packaging material has a  
25           haze below 20%.

22. A packaged product according to Claim 21,

wherein the hydrophilic gas-barrier resin is ethylene-vinyl alcohol copolymer.

23. A packaged product according to Claim 21,  
5 wherein the hydrophilic gas-barrier resin is glycolic acid (co-)polymer.

24. A packaged product according to any of  
Claims 19 to 23, wherein the packaged material has  
10 been subjected to a heat-shrinking treatment during the heat treatment.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/02431

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L2/04 A23L3/02 A23L3/10 B65B55/10 A23B4/005  
A23C3/023 A61L2/26

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L A23L B65B A23B A23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 022 913 A (HASEGAWA TOMOHISA ET AL) 8 February 2000 (2000-02-08) column 3, line 26-59 column 7, line 8 -column 8, line 35 column 10, line 28 -column 11, line 29 column 31, line 5-51 ----	1-24
X	EP 1 176 002 A (KUREHA CHEMICAL IND CO LTD) 30 January 2002 (2002-01-30) paragraphs '0001!', '0012!', '0020!', '0021! ----	19-24
X	US 4 818 592 A (OSSIAN WILLIAM F) 4 April 1989 (1989-04-04) column 1, line 64 -column 3, line 68 ----	19-24
X	US 4 355 721 A (KNOTT II JACK E ET AL) 26 October 1982 (1982-10-26) column 2, line 8 -column 429 -----	19-24

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

27 May 2003

Date of mailing of the international search report

04/06/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Pers1ch1n1, C

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 03/02431

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6022913	A	08-02-2000	AU 733245 B2	10-05-2001
			AU 4135597 A	26-03-1998
			BR 9706701 A	08-09-1999
			CN 1347933 A	08-05-2002
			CN 1200698 A ,B	02-12-1998
			EP 0890432 A1	13-01-1999
			WO 9809813 A1	12-03-1998
			JP 10128923 A	19-05-1998
			US 6143384 A	07-11-2000
			JP 10237180 A	08-09-1998
EP 1176002	A	30-01-2002	AU 2461500 A	29-08-2000
			EP 1176002 A1	30-01-2002
			CN 1340002 T	13-03-2002
			WO 0047406 A1	17-08-2000
US 4818592	A	04-04-1989	US 4640852 A	03-02-1987
			DK 551785 A	29-05-1986
			EP 0183512 A2	04-06-1986
			GR 852868 A1	31-03-1986
			JP 61179737 A	12-08-1986
			NO 854731 A	29-05-1986
			SE 8505546 A	29-05-1986
			US 5154789 A	13-10-1992
US 4355721	A	26-10-1982	AU 554081 B2	07-08-1986
			AU 7345181 A	09-09-1982
			AU 533431 B2	24-11-1983
			AU 5832580 A	13-11-1980
			DE 3018118 A1	19-03-1981
			DE 8012849 U1	12-03-1981
			FR 2456052 A1	05-12-1980
			GB 2048775 A ,B	17-12-1980
			HK 68285 A	20-09-1985
			JP 56004571 A	17-01-1981
			MY 76685 A	31-12-1985
			SG 45384 G	08-03-1985